Contribution from the Department of Chemistry,
The University of Michigan, Ann Arbor, Michigan 48104

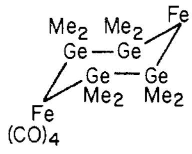
Synthesis of Five- and Six-Membered Iron–Germanium Heterocycles: *cyclo*-1,4-Bis(tetracarbonyliron)-2,3,5,6-Tetrakis(dimethylgermanium) and *cyclo*-1,3-Bis(tetracarbonyliron)-2,4,5-Tris(dimethylgermanium)

Kelly Triplett and M. David Curtis*

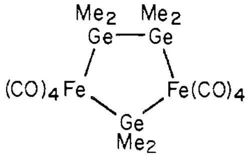
Received February 12, 1975

AIC50104C

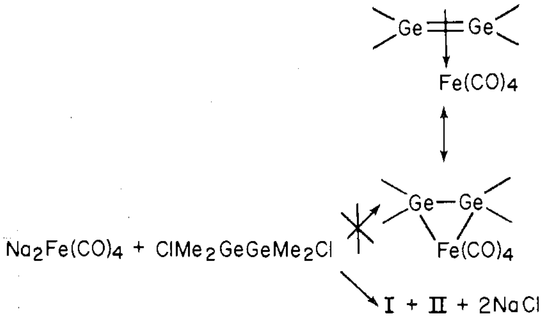
In our continuing investigation[1-4] of possible means to stabilize ($p\pi$–$p\pi$) bonds to silicon and germanium, we have isolated the novel heterocyclic compounds, *cyclo*-1,4-bis(tetracarbonyliron)–2,3,5,6-tetrakis(dimethylgermanium) and *cyclo*-1,3-bis(tetracarbonyliron)–2,4,5-tris(dimethylgermanium), I and II, respectively. These compounds were obtained during an attempt to synthesize a metal carbonyl-stabilized resonance extreme of a Ge=Ge double bond as shown in eq 1.



I



II



(1)

Experimental Section

All manipulations were carried out under dry nitrogen using standard Schlenck-ware techniques.[5] Melting points were obtained in evacuated capillaries.

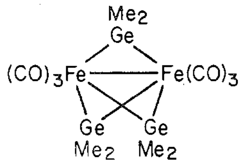
Synthesis of I and II. $Na_2Fe(CO)_4$ (1.5 g, 5.7 mmol) was slurried in 50 ml of petroleum ether (bp 30-60°) and 1,2-dichlorotetramethyldigermane (1.6 g, 5.8 mmol) was then added with the exclusion of light. (Light was also excluded as much as possible in all the following manipulations.) After stirring overnight, during which time the color had changed from red to yellow, the mixture was filtered and the filtrate concentrated to a volume of ca. 15 ml to give white crystals shown to be II. The supernatant liquid was removed with a syringe and placed in another Schlenck tube. An equal volume of methanol was added and much of the petroleum ether was removed under reduced pressure. Cooling to −78° gave white to pale yellow crystals of I.

Compound I melts at 175–176° and displays carbonyl absorptions in petroleum ether at 2048 m, 2001 s, 1992 s, and 1983 sh cm^{-1}. The NMR in C_6H_6 consists of a singlet at τ 9.18, and a parent ion at *m/e* 746 is observed in the mass spectrum. Anal. Calcd for $C_{16}H_{24}Fe_2Ge_4O_8$: C, 25.72; H, 3.22. Found: C, 25.89; H, 3.34.

Compound II melts at 302° dec and shows carbonyl absorptions at 2040 m, 2000 s, and 1985 m cm^{-1} in petroleum ether. The NMR in C_6H_6 has singlets at τ 9.23 and 8.75 in a 2:1 area ratio; *m/e* of the parent occurs at 644. Anal. Calcd for $C_{14}H_{18}Fe_2Ge_3O_8$: C, 26.10; H, 2.80. Found: C, 26.23; H, 2.93.

Results and Discussion

The interaction of $Na_2Fe(CO)_4$ with $ClMe_2GeGeMe_2Cl$ gives initially a red solution which then turns yellow. From the yellow solution, compounds I and II are obtained. When pure, these complexes are colorless, but are often obtained as pale yellow solids due to contamination by $(CO)_3Fe(\mu\text{-}GeMe_2)_3Fe(CO)_3$ (III) (see below). Compound III was previously synthesized by Brooks et al. from Me_2GeH_2 and $Fe_2(CO)_9$.[6]



III

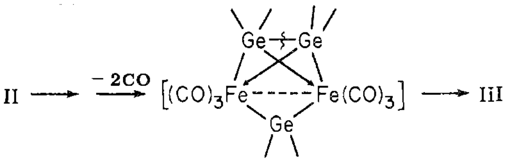
The use of more polar solvents, e.g., THF, gives poor yields of I and correspondingly higher yields of II, irrespective of the order of addition of reagents or the temperature.

The structure of I is undoubtedly analogous to the recently reported, isoelectronic complex, $[(CO)_4Cr]_2(AsMe_3)_4$ (IV),[7] which was shown by X-ray analysis to possess a cyclohexane chain conformation. As with IV, only a single NMR peak was observed down to −90°, at which point the solubility limit and viscosity broadening were reached. Thus, the interconversion of methyl groups by chair flipping must be rapid on the NMR time scale.

Compound II is assigned the five-membered ring structure on the basis of its NMR spectrum (two Me peaks in ratio of 2:1) and its IR which is similar to other $E_2Fe(CO)_4$ type structures with local C_{2v} symmetry.[8] The formation of II is somewhat surprising since a germanium–germanium bond was necessarily cleaved in its formation, and Noltes and Bulten have shown that hexamethyldigermane is insensitive to cleavage even by alkali metals.[9] II does not arise from I by a photochemical reaction since II is obtained in about 50% yield even in the absence of light.

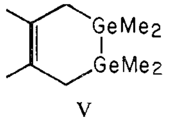
Both I and II in solution rapidly produce III when exposed to uv light. Even sunlight or fluorescent light causes a rapid yellowing of their solutions. In the transformation of I or II to III, a Ge–Ge bond is ruptured and since these bonds are not photosensitive under normal conditions, it is likely that the first step in the photolysis of I or II involves loss of carbonyl to form a coordinatively unsaturated metal.[10,11]

Rearrangements of the Ge–Ge bonds, as shown schematically for II, can then complete the 18 electron configuration on each Fe.



On going from I to III, a dimethylgermylene (Me_2Ge) group is necessarily lost and a peak at τ 9.63, observed in the photolysis reaction mixture from I, may correspond to cyclic $(Me_2Ge)_n$ (n = 5 or 6). Due to the small quantities, this substance was not isolated, however.

Several attempts were made to generate $Me_2Ge{=}GeMe_2$ by Ce(IV) or Fe(III) oxidation of I in the presence of trapping agents, e.g., 2,3-dimethylbutadiene or cyclopentadiene. Under a variety of experimental conditions, e.g., temperature, solvent, mode of addition of reagents, etc., no evidence for compounds, e.g., V, was obtained. The observed products were unreacted I and an insoluble, green residue which could not be adequately characterized, but did not contain the trapping agent.



V

Acknowledgment. The authors thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

Registry No. I, 55669-46-0; II, 55669-47-1; $Na_2Fe(CO)_4$, 14878-31-0; 1,2-dichlorotetramethyldigermane, 22702-77-8.

References and Notes

(1) R. C. Job and M. D. Curtis, *Inorg. Chem.*, **12**, 2510 (1973).
(2) J. V. Scibelli and M. D. Curtis, *J. Organomet. Chem.*, **40**, 317 (1972).
(3) M. D. Curtis, *J. Am. Chem. Soc.*, **91**, 6011 (1969).
(4) M. D. Curtis, *J. Organomet. Chem.*, **60**, 63 (1973).
(5) D. F. Shriver, "The Manipulation of Air-Sensitive Compounds", McGraw-Hill, New York, N.Y., 1968.
(6) E. H. Brooks, M. Elder, W. A. G. Graham, and D. Hall, *J. Am. Chem. Soc.*, **90**, 3587 (1968).
(7) F. A. Cotton and T. R. Webb, *Inorg. Chim. Acta*, **10**, 127 (1974).
(8) F. T. Delbecke, E. G. Claeys, G. P. van der Kelen, and Z. Eeckhaut, *J. Organomet. Chem.*, **25**, 213 (1970).
(9) J. G. Noltes and E. J. Bulten, *J. Organomet. Chem.*, **11**, 119 (1968).
(10) W. Strohmeier, *Angew. Chem., Int. Ed. Engl.*, **3**, 730 (1964).
(11) R. C. Job and M. D. Curtis, *Inorg. Chem.*, **12**, 2514 (1973).

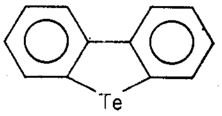
Contribution No. 3458 from the Department of Chemistry,
University of California, Los Angeles, California 90024

Dibenzotellurophene. A New Synthesis by Way of 2-Biphenylyltellurium Trichloride

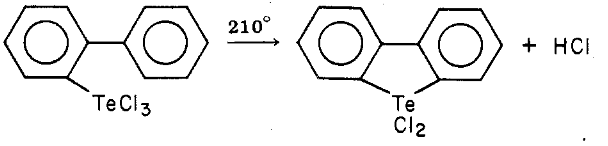
J. D. McCullough

Received February 12, 1975 AIC50106X

Several syntheses of dibenzotellurophene, I, have been reported. The two earliest methods[1,2] give very poor yields and the procedures require close attention for long periods. More recently, two syntheses[3] have been reported to give good yields in the final steps, but since the starting materials are not readily available, additional time and effort would be required for their preparation. The procedure which gives good yields of dibenzoselenophene[4] cannot be applied directly to the tellurium compound because the preparation of useful quantities of potassium tellurocyanate, KTeCN, in aqueous solution appears to be impossible.[5] In spite of this difficulty, a ring-closing step similar to that in the dibenzoselenophene synthesis is useful here, namely, the spontaneous conversion of 2-biphenylyltellurium trichloride, II, at ~210° to dibenzotellurophene dichloride, III, which proceeds in quantitative yield. The dichloride is reduced to dibenzotellurophene by potassium pyrosulfite, $K_2S_2O_5$.



I



(1)

II III

The previously unreported 2-biphenylyltellurium trichloride was prepared by two different methods. One of these was patterned after the procedure used by Campbell and Turner[6] for the preparation of some phenoxatellurin derivatives. While several steps are involved, each is fairly easy to carry out in reasonably good yield. As applied to the dibenzotellurophene synthesis, the steps take the form of eq 2–4 in which the symbol Ar represents the 2-biphenylyl group. The second method involves reactions 5 and 6. While the latter procedure is more direct, the reaction conditions (rigorous exclusion of moisture and oxygen) are more exacting and the yields are poorer, probably due in part to the fact that some of the $ArTeCl_3$ already formed also reacts with ArLi to give Ar_2TeCl_2, etc. In fact, Wittig and Fritz[7] have used a similar reaction to prepare tetraphenyltellurium.

$$ArNH_2 \xrightarrow[NaNO_2]{H_2SO_4} ArN_2^+ \xrightarrow[HgCl_2]{HCl} (ArN_2)_2Hg_2Cl_6 \qquad (2)$$

$$(ArN_2)_2Hg_2Cl_6 \xrightarrow[-60°]{Cu\ in\ (CH_3)_2CO} ArHgCl + N_2 + CuCl \qquad (3)$$

$$ArHgCl + TeCl_4 \xrightarrow[reflux]{CHCl_3} ArTeCl_3 + HgCl_2 \qquad (4)$$

$$ArBr + n\text{-}BuLi \xrightarrow[-60°]{Et_2O} ArLi + n\text{-}BuBr \qquad (5)$$

$$ArLi + TeCl_4 \xrightarrow{Et_2O} ArTeCl_3 + LiCl \qquad (6)$$

Preparations of dibenzotellurophene dibromide and dibenzotellurophene diiodide are also described.

Experimental Section

Physical Measurements. Melting points were measured in open capillaries and are uncorrected. All of the halogenated tellurium compounds reported here decompose appreciably before melting. In these cases the recorded melting points were taken on samples immersed in the bath about 5° below the recorded value. Microanalyses were carried out by Miss Heather King in this department. X-Ray diffraction data on two of the compounds were taken on the Syntex $P\bar{1}$ autodiffractometer.

Materials. All chemicals and solvents used were reagent grade except as noted below. 2-Aminobiphenyl (Eastman, practical grade), 2-bromobiphenyl (K and K Laboratories), and tellurium tetrachloride (Alfa Inorganics) were used without further purification. Diethyl ether was dried over sodium and distilled as needed under N_2 atmosphere. Acetone was dried over Linde Molecular Sieves, Type A, and chloroform was passed through a column of active basic aluminum oxide (EM Laboratories, Activity I) to remove water and methanol. *n*-Butyllithium (Alfa Inorganics) was in the form of a 2.2 *M* solution in hexane.

2-Biphenylylmercury Chloride. A solution of 34 g (0.20 mol) of 2-aminobiphenyl in 30 ml of warm concentrated sulfuric acid was added with stirring to 1.0 l. of ice water. A solution of 14 g (0.20 mol) of sodium nitrite in 25 ml of cold water was then slowly added to the mechanically stirred amine bisulfate solution. After about 10 min, the diazotized amine solution was added in small (5–10 ml) increments to a mechanically stirred solution of 54 g (0.20 mol) of mercury(II) chloride in 60 ml of concentrated hydrochloric acid and 50 g of ice in a 2-l. beaker. The finely divided pale yellow precipitate was filtered off and washed twice with water, then with absolute ethanol, and finally with anhydrous ether.

The diazonium salt, formulated here as $(C_{12}H_9N_2)_2Hg_2Cl_6$, was placed in a 1-l. conical flask, mixed well with 400 ml of anhydrous acetone and cooled externally with Dry Ice to ca. −60°. Copper powder was prepared by adding 26 g (0.40 mol) of zinc dust in ~0.5-g portions to a mechanically stirred solution of 125 g (0.50 mol) of $CuSO_4 \cdot 5H_2O$ in 400 ml of freshly boiled water. The filtered copper powder was washed with water and then with dry acetone and stirred into the diazonium salt–acetone mixture. The flask was loosely covered with an inverted beaker and packed in Dry Ice in a well insulated container so that the reaction mixture would remain at ca. −60° for 24–36 hr; then it was allowed slowly to warm up to room temperature. After evolution of nitrogen gas had stopped, the mixture was filtered and the residue was extracted with two 100-ml portions of hot acetone. The extracts and filtrate were combined and concentrated to approximately 200 ml and the product was allowed to crystallize out at 0°. Recrystallization from ethanol gave 27 g (0.069 mol, 35% yield) of white needles, mp 167.5°.[8]

2-Biphenylyltellurium Trichloride, II. Method I. A solution of 11.3 g (29.1 mmol) of 2-biphenylylmercury chloride and 7.84 g (29.1 mmol) of tellurium tetrachloride in 90 ml of dry (methanol-free) chloroform was refluxed for 1.25 hr. After cooling of the mixture